

Thermodynamics of heterogeneous crystal nucleation in contact and immersion modes

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Abstract

One of most intriguing problems of heterogeneous crystal nucleation in droplets is its strong enhancement in the contact mode (when the foreign particle is presumably in some kind of *contact* with the droplet surface) compared to the immersion mode (particle *immersed* in the droplet). Many heterogeneous centers have different nucleation thresholds when they act in contact or immersion modes, indicating that the mechanisms may be actually different for the different modes. Underlying physical reasons for this enhancement have remained largely unclear. In this paper we present a model for the thermodynamic enhancement of heterogeneous crystal nucleation in the contact mode compared to the immersion one. To determine if and how the surface of a liquid droplet can thermodynamically stimulate its heterogeneous crystallization, we examine crystal nucleation in the immersion and contact modes by deriving and comparing with each other the reversible works of formation of crystal nuclei in these cases. As a numerical illustration, the proposed model is applied to the heterogeneous nucleation of Ih crystals on generic macroscopic foreign particles in water droplets at $T = 253$ K. Our results show that the droplet surface does thermodynamically favor the contact mode over the immersion one. Surprisingly, our numerical evaluations suggest that the line tension contribution to this enhancement from the contact of three water phases (vapor-liquid-crystal) may be of the same order of magnitude as or even larger than the surface tension contribution.

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1 Introduction

The size, composition, and phases of aerosol and cloud particles affect the radiative and chemical properties^{1,2} of clouds and hence have a great impact on Earth's climate as a whole. On the other hand, the composition, size, and phases of atmospheric particles are determined by the rate at and mode in which these particles form and evolve.²⁻⁴

Water constitutes an overwhelmingly dominant chemical species that participates in atmospheric processes. Consequently, great importance is attributed to studying aqueous aerosols and cloud droplets as well as their phase transformations. In a number of important cases atmospheric particles appear to freeze homogeneously.⁴⁻⁶ For example, the conversion of supercooled water droplets into ice at temperatures below about -30°C is known to occur homogeneously, mainly because the concentrations of the observed ice particles in the clouds often exceed the number densities of preexisting particles capable of nucleating ice.^{4,5} Also, it has been suggested that aqueous nitric acid-containing cloud droplets in the polar stratosphere freeze into nitric acid hydrates via homogeneous nucleation.⁶ Understanding how nitric acid clouds form and grow in the stratosphere is a topic of current interest because such clouds participate in the heterogeneous chemistry that leads to springtime ozone depletion over the polar regions.²

However, most phase transformations in aqueous cloud droplets occur as a result of heterogeneous nucleation on preexisting macroscopic particles, macromolecules, or even ions.³ Heterogeneous nucleation of ice on a microscopic foreign particle can be considered as the adsorption of water molecules on a substrate which serves as a template. If the water molecules adsorb in a configuration close enough to the crystalline structure of ice, then the energy barrier between phases is substantially reduced. Recent work on the heterogeneous nucleation of ice in the atmosphere is motivated by the evidence, primarily from modeling studies, that heterogeneous freezing may significantly impact the radiative properties, both in the visible and infrared, of

cirrus clouds. The leading candidates for heterogeneous nucleating centers are the mineral dusts (fly ash and metallic particles) and emissions from aircraft, primarily soot.⁷⁻⁹ Interest in cirrus clouds motivated several laboratory studies as well.^{10,11} They showed that the presence of various foreign inclusions shifts the apparent freezing temperature of droplets upward by as much as 10°C.

Most investigators targeted particulates as the primary heterogeneous ice nucleating centers in the atmosphere. Recently, however, increasing attention is paid to the role of films of high-molecular-weight organic compounds located on droplets. Such compounds are emitted into the atmosphere, especially in regions that are influenced by biomass burning.¹² It was reported, for example, that the films of long-chain alcohols and some other organic species can catalyze ice nucleation in droplets at a supercooling of only 1°C.^{13,14}

So far, the physical mechanism underlying heterogeneous crystal nucleation in droplets remains rather obscure.² As an additional mystery, many heterogeneous centers have different nucleation thresholds when they act in different modes - contact or immersion, indicating that the mechanisms may be actually different for the different modes. In the contact mode, the ice-nucleating particle contacts water droplet, i.e., touches or intersects its surface. whereas in the immersion mode the particle is immersed in the water droplet (Figure 1).^{2,15} The same particle tends to trigger the freezing of an supercooled water droplet at a higher temperature in the contact mode than in the immersion one.^{2,15,16}

The cause of this enhancement is unknown, but it provides a hint that the water surface could be of special interest in ice nucleation. Several investigators have put forward conjectures on the mechanism of contact nucleation, all of which depend on the contact of a particle impinging upon the droplet surface from air.² One of the hypothesis is based on the partial solubility of small solid particles whereby active sites at the surface of a particle are subject to erosion

after it becomes immersed in water.^{17,18} Another hypothesis suggests¹⁹ that only those particles enhance nucleation in the contact mode which exhibit a strong affinity for water. During the initial contact with the droplet (*before* the equilibrium adsorption is achieved) such particles might strongly lower the free energy barrier to ice nucleation at its surface. Another interesting explanation²⁰ suggests that the contact mode enhancement of crystal nucleation is due to the mechanically forced rapid spreading of water along the hydrophobic solid surface which forces its local wetting and thereby temporarily creates local high interface-energy zones increasing the probability of crystal nucleation. While acceptable for some particular cases, all those explanations have some inconsistencies and limitations, and so far no rigorous (and general enough) theoretical model of this phenomenon has been proposed.

As a related problem, recently a thermodynamic theory was developed^{21,22} that prescribes the condition under which the surface of a droplet can stimulate *homogeneous* crystal nucleation therein so that the homogeneous formation of a crystal nucleus with one of its facets at the droplet surface (surface-stimulated mode) is thermodynamically favored over its formation with all the facets *within* the liquid phase (volume-based mode). For both unary and multicomponent droplets the inequality coincides with the condition for the partial wettability of at least one of the facets of a crystal nucleus by its own melt.²³ This effect was experimentally observed for several systems,^{24,25} including water-ice²⁶ at temperatures at or below 0°C.

Clearly, the mode of crystal nucleation is most likely determined by both thermodynamic and kinetic factors. However, the partial wettability of a solid by its melt may help to explain why, in molecular dynamics simulations of various kinds of supercooled liquid droplets^{27,28} the crystal nuclei appear preferentially close to the surface. Since smaller droplets have a higher surface-to-volume ratio, the per-droplet nucleation rates in small droplets tend to be higher than in the bulk. Hence it is experimentally easier to observe the crystallization of aerosols,

having a large collective surface area, than those having a large volume. Recent experiments¹⁶ on the heterogeneous freezing of water droplets in both immersion and contact modes have also provided evidence that the rate of crystal nucleation in the contact mode is much higher because the droplet surface may stimulate heterogeneous crystal nucleation in a way similar to the enhancement of the homogeneous process.

In this paper we extend the approach, previously developed in refs.21,22, to heterogeneous crystal nucleation on a solid particle (in both immersion and contact modes) and present a thermodynamic model thereof. Our thermodynamic analysis suggests that, indeed, the droplet surface can thermodynamically enhance crystal nucleation in the contact mode compared to the immersion mode. Whether this occurs or not for a particular foreign particle is determined, however, by the interplay between five surface tensions and four line tensions involved in this process.

The paper is structured as follows. In section 2 we derive and compare with each other the expressions for the free energy of heterogeneous formation of a crystal nucleus on a solid (say, dust) particle in the immersion and contact modes. For the sake of simplicity, in this work we consider only unary systems, i.e., pure water droplets, but the generalization to multicomponent droplets can be carried out as well. Only one kind of foreign nucleating centers is considered, namely, those completely wettable by water. Numerical predictions and possible experimental verification of the model are discussed in Section 3. The results and conclusions are summarized in section 4.

2 Free energy of heterogeneous formation of crystal nuclei in contact and immersion modes

To determine if and how the surface of a liquid droplet can thermodynamically stimulate its heterogeneous crystallization, it is necessary to consider the formation of a crystal cluster in the two modes (Figure 1). In the “immersion” mode, the crystal cluster is formed with one of its facets on a foreign particle that is completely immersed in a liquid droplet; all other crystal facets interface the liquid. In the “contact” mode, the foreign particle touches (i.e., is in contact with) the droplet surface and the cluster forms with one of the crystal facets on the particle (as in the immersion mode), another facet at the liquid-vapor interface, and all other facets making the “crystal-liquid” interface. In these two cases the reversible works of formation of a crystal nucleus (critical cluster) should be derived and compared with each other. This can be carried out in the framework of the classical nucleation theory (CNT) for both unary and multicomponent droplets. In this paper we consider the crystallization of unary droplets.

The droplet surface can incur some deformation if its crystallization is initiated at its surface. The thermodynamic analysis of the case where the crystallization begins at a droplet surface can be considerably more complicated when compared to the case where it forms at the surface of a bulk liquid. However, one can show²¹ that if $a_1/\pi R^2 \ll 1$ (where a_1 is the surface area of the crystal facet interfacing the vapor and R is the droplet radius), the formation of a crystal at a droplet surface can be considered as crystallization at the surface of a *bulk* liquid. Under conditions relevant to the freezing of atmospheric droplets, crystal nuclei are usually of sub- or nanometer size, while the droplets themselves are in submicron to micrometer size range, i.e., the above condition is well satisfied. Since the analysis of the freezing of atmospheric droplets is our ultimate goal, one can assume the droplet surface to be flat and thus avoid the complexity

of taking into account the droplet deformation upon freezing. Besides, heterogeneous particles serving as nucleating centers can be considered as macroscopic particle of linear sizes much greater than the crystal nuclei hence the part of its surface on which the crystal nucleus forms can be considered to be flat as well.

Let us consider a single-component bulk liquid. A macroscopic heterogeneous particle is either completely immersed in the liquid or in contact with the liquid-vapor interface. Crystallization will take place in this liquid if it is in a metastable (supercooled) state. The reversible work of crystal formation, W , can be found as the difference between X_{fin} , the appropriate thermodynamic potential of the system in its final state (liquid+crystal), and X_{in} , the same potential in its initial state (liquid): $W = X_{fin} - X_{in}$. Since the density of the liquid may be different from that of the solid, the volume of the liquid may change upon crystallization if the process is not constrained to be conducted at constant volume. In such a case, strictly speaking, one cannot calculate W as the difference in the Helmholtz free energies since the volume work that the entire system exchanges with the environment should not be regarded as work involved in the formation of a local nucleus. As an approximation, the use of the Helmholtz free energy is still acceptable since, in the thermodynamic limit, the change in the total volume of the system is usually negligible. A better choice for the thermodynamic potential is the Gibbs free energy if the system is in contact with a pressure reservoir (since the unconnected volume work exchanged with the environment is automatically removed from the Gibbs free energy). However,²⁹ in the thermodynamic limit, the use of either the Gibbs or Helmholtz free energy or grand thermodynamic potential is acceptable for the evaluation of W .

Neglecting the density difference between liquid and solid phases and assuming the crystallization process to be isothermal, one can say that the total volume, the temperature, and the number of molecules in the system, respectively, will be constant. Thus the reversible work of

formation of a crystal embryo can be evaluated as the difference between F_{fin} , the Helmholtz free energy of the system in its final state (liquid+crystal+foreign particle), and F_{in} , in its initial state (liquid+foreign particle):

$$W = F_{fin} - F_{in}. \quad (1)$$

2.1 Foreign particle completely immersed in the liquid

Consider a bulk liquid in a container whose upper surface is in contact with the vapor phase of constant pressure and temperature. A macroscopic foreign particle is completely immersed in this liquid. Clearly, for this system to be in mechanical and thermodynamic equilibrium, the particle must be completely wettable by the liquid. Upon sufficient supercooling, a crystal nucleus may form heterogeneously with one of its facets on the foreign particle. The crystal is considered to be of arbitrary shape with λ facets (Figure 2). We will assign the subscript “ λ ” to the facet which is in contact with the foreign particle.(Figure 3)

Let us introduce the superscripts α , β , γ and δ to denote quantities in the liquid, vapor, crystal nucleus, and foreign particle, respectively. Double superscripts will denote quantities at the corresponding interfaces, and triple superscripts at the corresponding three-phase contact lines. The surface area and surface tension of facet i ($i = 1, \dots, \lambda$) will be denoted by A_i and σ_i , respectively. (Anisotropic interfacial free energies are believed to be particularly important in determining the character of the nucleation process.) Hereafter, we adopt the definition of the surface tension of a solid, σ^{solid} , as given in chapter 17 of ref.19. Namely, $\sigma^{solid} = f' + \sum_i \Gamma_i \mu'_i$, where f' , Γ , and μ' are the surface free energy per unit area, adsorption, and chemical potential of component i , all attributed to the dividing surface between solid and fluid. In the following, we will neglect the adsorption at the solid-fluid interfaces. Thus, by definition, the surface tension of the solid will be equal to the surface free energy per unit area.

Let us denote the number of molecules in the crystal cluster by ν . Neglecting the density change upon freezing and assuming the equality of pressures in the vapor and liquid, $P^\alpha = P^\beta$, the reversible work of heterogeneous formation of the crystal (with its facet λ on the foreign particle) is given by the expression

$$W^{imm} = \nu[\mu^\gamma(P^\gamma, T) - \mu^\alpha(P^\alpha, T)] - V^\gamma(P^\gamma - P^\alpha) + \sum_{i=1}^{\lambda-1} \sigma_i^{\alpha\gamma} A_i^{\alpha\gamma} + \sigma_\lambda^{\gamma\delta} A_\lambda^{\gamma\delta} - \sigma^{\alpha\delta} A_\lambda^{\gamma\delta} + \tau^{\alpha\gamma\delta} L^{\alpha\gamma\delta}, \quad (2)$$

where μ , P , V , and T are the chemical potential, pressure, volume, and temperature, respectively, and τ is the line tension associated with a three-phase contact line³⁰ of length L .

The necessary and sufficient conditions for the equilibrium shape (known as the Wulff form) of the crystal are represented by a series of equalities referred to as Wulff's relations (see, e.g., ref.23), which can be regarded as a series of equilibrium conditions on the crystal "edges" formed by adjacent facets. For example, on the edge between homogeneously formed facets i and $i+1$ the equilibrium condition is

$$\frac{\sigma_i^{\alpha\gamma}}{h_i} = \frac{\sigma_{i+1}^{\alpha\gamma}}{h_{i+1}} \quad (i = 1, \dots, \lambda), \quad (3)$$

where h_i is the distance from facet i to a point O within the crystal (see Figure 2) resulting from the Wulff construction.²³

In the case when one of the facets (facet λ) is the crystal-vapor interface while all the others lie within the liquid phase (see Figure 3), the equilibrium conditions on the edges formed by this facet with the adjacent ones (hereafter marked by a subscript j) are given by

$$\frac{\sigma_j^{\alpha\gamma}}{h_j} = \frac{\sigma_\lambda^{\gamma\delta} - \sigma^{\alpha\delta}}{h_\lambda}. \quad (4)$$

Note that the height of the λ -th pyramid (constructed with the base on facet λ and with the apex at point O of the Wulff crystal) will differ from that with all of the facets in the liquid. Thus, the shape of the crystal will differ from that in which all facets are in contact with the

liquid. For this case, Wulff's relations take the form

$$\frac{\sigma_1^{\alpha\gamma}}{h_1} = \frac{\sigma_2^{\alpha\gamma}}{h_2} = \dots = \frac{\sigma_\lambda^{\alpha\gamma} - \sigma^{\alpha\delta}}{h_\lambda} \quad (5)$$

(see also refs.21,22). In the above consideration, it is assumed that the mechanical effects within the crystal (e.g., stresses) reduce to an isotropic pressure P^γ . In this case²¹

$$P^\gamma - P^\alpha = \frac{2\sigma_i^{\alpha\gamma}}{h_i} \quad (i = 1, \dots, \lambda - 1), \quad P^\gamma - P^\alpha = \frac{2(\sigma_\lambda^{\gamma\delta} - \sigma^{\alpha\delta})}{h_\lambda}. \quad (6)$$

Equation (6) applied to the crystal is the equivalent of Laplace's equation applied to liquid. Thus, just as for a droplet, one can expect to find a high pressure within a small crystal. It is this pressure that is the cause of the increase in the chemical potential within the crystal.

Note that the line tension contributions to the free energy of crystal formation were omitted in the model for homogeneous crystal nucleation in the surface-stimulated mode^{21,22} because they were assumed to be negligible compared to the volume and surface contributions. However, this assumption may no longer be valid for heterogeneous crystal nucleation because the nucleus is now much smaller (compared to the homogeneously formed one) and hence the contributions of three-phase contact lines can be more important.³¹⁻³³

Making use of equations (5) and (6), one can rewrite eq.(2) as

$$W^{imm} = \nu[\mu^\gamma(P^\alpha, T) - \mu^\alpha(P^\alpha, T)] + \sum_{i=1}^{\lambda-1} \sigma_i^{\alpha\gamma} A_i^{\alpha\gamma} + \sigma_\lambda^{\gamma\delta} A_\lambda^{\gamma\delta} - \sigma^{\alpha\delta} A_\lambda^{\gamma\delta} + \tau^{\alpha\gamma\delta} L^{\alpha\gamma\delta}. \quad (7)$$

In this equation, the first term represents the excess Gibbs free energy of the molecules in the crystal compared to their Gibbs free energy in the liquid state. This term is related to the enthalpy of fusion Δh by (see, e.g., ref. 23)

$$\mu^\gamma(P^\alpha, T) - \mu^\alpha(P^\alpha, T) = - \int_{T_0}^T \Delta h \frac{dT'}{T'}, \quad (8)$$

where T_0 is the melting temperature of the bulk solid ($T < T_0$), and $\Delta h < 0$.

If the supercooling $T - T_0$ is not too large or, alternatively, if in the temperature range between T and T_0 the enthalpy of fusion does not change significantly, eq.(8) takes the form

$$\mu^\gamma(P^\alpha, T) - \mu^\alpha(P^\alpha, T) = -\Delta h \ln \Theta. \quad (9)$$

with $\Theta = T/T_0$. Thus, one can rewrite eq.(7) in the following form

$$W^{imm} = -\nu \Delta h \ln \Theta + \sum_{i=1}^{\lambda-1} \sigma_i^{\alpha\gamma} A_i^{\alpha\gamma} + \sigma_\lambda^{\gamma\delta} A_\lambda^{\gamma\delta} - \sigma^{\alpha\delta} A_\lambda^{\gamma\delta} + \tau^{\alpha\gamma\delta} L^{\alpha\gamma\delta}. \quad (10)$$

By definition, the critical crystal (i.e., nucleus) is in equilibrium with the surrounding melt. For such a crystal the first term in eq.(2) vanishes. On the other hand, for a crystal with one of its facets being a crystal-foreign particle interface, and the others interfaced with the liquid, one can show that

$$V^\gamma(P^\gamma - P^\alpha) = \frac{2}{3} \left(\sum_{i=1}^{\lambda-1} \sigma_i^{\alpha\gamma} A_i^{\alpha\gamma} + \sigma_\lambda^{\gamma\delta} A_\lambda^{\gamma\delta} - \sigma^{\alpha\delta} A_\lambda^{\gamma\delta} \right). \quad (11)$$

(This equality can be derived by representing V^γ as the sum $\frac{1}{3} \sum_{i=1}^{\lambda} h_i A_i$ of the volumes of λ pyramids with their bases at the crystal facets and their apexes at point O. The difference $P^\gamma - P^\alpha$ for every term in this sum is replaced by the RHS of the corresponding equality in eq.(6).) Substituting eq.(11) into eq.(2), one can thus obtain the following expression for the reversible work W_*^{imm} of formation of a critical crystal:

$$W_*^{imm} = \frac{1}{3} \left(\sum_{i=1}^{\lambda-1} \sigma_i^{\alpha\gamma} A_i^{\alpha\gamma} + \sigma_\lambda^{\gamma\delta} A_\lambda^{\gamma\delta} - \sigma^{\alpha\delta} A_\lambda^{\gamma\delta} \right) + \tau^{\alpha\gamma\delta} L^{\alpha\gamma\delta}, \quad (12)$$

or, alternatively,

$$W_*^{imm} = \frac{1}{2} V_*^\gamma (P_*^\gamma - P^\alpha) + \tau^{\alpha\gamma\delta} L^{\alpha\gamma\delta} \quad (13)$$

(hereafter the subscript “*” indicates the quantities for the nucleus; it is omitted on the RHS of expressions for W_*^{imm} to avoid the overcrowding of indices)

Clearly, in the atmosphere the crystal cluster forms not in the bulk liquid, but within a liquid droplet (see Figure 1) which is itself surrounded by a vapor phase. The reasoning here is

almost identical to the preceding if, again, we neglect the density difference between the liquid and crystal phases. One can easily show that all above equations, starting with eq.(2) and including eqs.(12) and (13) for the reversible work W_*^{imm} of formation of the critical crystal, remain valid except that the pressures in the liquid and vapor phases are not equal but are related by the Laplace equation $P^\alpha = P^\beta + 2\sigma^{\alpha\beta}/R$, with R being the radius of the droplet (assumed to remain constant during freezing).

2.2 Foreign particle in contact with the liquid-vapor interface

Now let us consider a foreign particle which is not immersed in a bulk liquid but is in some kind of contact with the liquid-vapor interface (Figures 1 and 4), with the vapor phase being at constant pressure and temperature. (Clearly, the particle must be completely wettable by the liquid in order for the same particle to be able to be in mechanical and thermodynamic equilibrium in both immersion and contact modes.) Now, upon sufficient supercooling, a crystal nucleus may form heterogeneously with one of its facets (marked with the subscript “ λ ”) on the foreign particle and another one at the vapor-liquid interface. The latter facet will be marked with the subscript $\lambda - 1$. All the other $\lambda - 2$ facets lie within the liquid phase.

Again, neglecting the density change upon freezing and the equality of pressures in the vapor and liquid, $P^\alpha = P^\beta$, the reversible work of heterogeneous formation of the crystal with its facet λ on the foreign particle, the facet $\lambda - 1$ interfacing vapor (i.e., in the contact mode) and all the others within the liquid phase will be given by the expression

$$\begin{aligned}
W^{con} = & \nu[\mu^\gamma(P^\gamma, T) - \mu^\alpha(P^\alpha, T)] - V'^\gamma(P^\gamma - P^\alpha) + \sum_{i=1}^{\lambda-2} \sigma_i^{\alpha\gamma} A_i^{\alpha\gamma} + \sigma_{\lambda-1}^{\beta\gamma} A_{\lambda-1}^{\beta\gamma} - \sigma^{\alpha\beta} A_{\lambda-1}^{\beta\gamma} + \\
& \sigma_\lambda^{\gamma\delta} A_\lambda^{\gamma\delta} - \sigma^{\alpha\delta} A_\lambda^{\gamma\delta} + \tau^{\alpha\beta\gamma} L^{\alpha\beta\gamma} + (\tau^{\beta\gamma\delta} - \tau^{\alpha\beta\delta}) L^{\beta\gamma\delta} + \tau^{\alpha\gamma\delta} L'^{\alpha\gamma\delta}.
\end{aligned} \tag{14}$$

Considering the contact mode, the prime will indicate quantities whereof the values may differ from those in the immersion mode. The equilibrium shape of the crystal (the Wulff form) is

again determined by a series of equilibrium conditions on the crystal “edges” formed by adjacent facets. For example, the equilibrium conditions on the edges formed by the facets $\lambda - 1$ and λ with the adjacent ones are given by

$$\frac{\sigma_j^{\alpha\gamma}}{h_j} = \frac{\sigma_{\lambda-1}^{\beta\gamma} - \sigma^{\alpha\beta}}{h'_{\lambda-1}} \quad (j \neq \lambda), \quad \frac{\sigma_k^{\alpha\gamma}}{h_k} = \frac{\sigma_\lambda^{\gamma\delta} - \sigma^{\alpha\delta}}{h_\lambda} \quad (k \neq \lambda - 1), \quad (15)$$

where j and k mark the facets adjacent to facets $\lambda - 1$ and λ , respectively, and primes will hereafter mark quantities for facet $\lambda - 1$ at the droplet surface. Note again that the height of the $\lambda - 1$ -th pyramid (constructed with the base on facet $\lambda - 1$ and with the apex at point O of the Wulff crystal) will differ from that with all of the facets (except for facet λ , see Figure 3) in the liquid. Thus, the shape of the crystal will differ from that formed heterogeneously in the immersion mode (i.e., when all facets, except for facet λ , are in contact with the liquid. For this case, Wulff’s relations take the form

$$\frac{\sigma_1^{\alpha\gamma}}{h_1} = \frac{\sigma_2^{\alpha\gamma}}{h_2} = \dots = \frac{\sigma_{\lambda-1}^{\alpha\gamma} - \sigma^{\alpha\beta}}{h'_{\lambda-1}} = \frac{\sigma_\lambda^{\alpha\gamma} - \sigma^{\alpha\delta}}{h_\lambda}. \quad (16)$$

Consequently, eq.(6) (the equivalent of Laplace’s equation applied to crystals) becomes

$$P^\gamma - P^\alpha = \frac{2\sigma_i^{\alpha\gamma}}{h_i} \quad (i = 1, \dots, \lambda - 2), \quad P^\gamma - P^\alpha = \frac{2(\sigma_{\lambda-1}^{\beta\gamma} - \sigma^{\alpha\beta})}{h_{\lambda-1}}, \quad P^\gamma - P^\alpha = \frac{2(\sigma_\lambda^{\gamma\delta} - \sigma^{\alpha\delta})}{h_\lambda}. \quad (17)$$

Making use of equations (16) and (17), one can rewrite eq.(14) as

$$\begin{aligned} W^{con} = & \nu[\mu^\gamma(P^\alpha, T) - \mu^\alpha(P^\alpha, T)] + \sum_{i=1}^{\lambda-2} \sigma_i^{\alpha\gamma} A_i^{\alpha\gamma} + \sigma_{\lambda-1}^{\beta\gamma} A_{\lambda-1}^{\beta\gamma} - \sigma^{\alpha\beta} A_{\lambda-1}^{\beta\gamma} + \sigma_\lambda^{\gamma\delta} A_\lambda^{\gamma\delta} - \sigma^{\alpha\delta} A_\lambda^{\gamma\delta} + \\ & \tau^{\alpha\beta\gamma} L^{\alpha\beta\gamma} + (\tau^{\beta\gamma\delta} - \tau^{\alpha\beta\delta}) L^{\beta\gamma\delta} + \tau^{\alpha\gamma\delta} L'^{\alpha\gamma\delta}. \end{aligned} \quad (18)$$

Furthermore, using eq.(9) one can represent eq.(18) in the following form

$$\begin{aligned} W^{con} = & -\nu\Delta h \ln \Theta + \sum_{i=1}^{\lambda-2} \sigma_i^{\alpha\gamma} A_i^{\alpha\gamma} + \sigma_{\lambda-1}^{\beta\gamma} A_{\lambda-1}^{\beta\gamma} - \sigma^{\alpha\beta} A_{\lambda-1}^{\beta\gamma} + \sigma_\lambda^{\gamma\delta} A_\lambda^{\gamma\delta} - \sigma^{\alpha\delta} A_\lambda^{\gamma\delta} + \\ & \tau^{\alpha\beta\gamma} L^{\alpha\beta\gamma} + (\tau^{\beta\gamma\delta} - \tau^{\alpha\beta\delta}) L^{\beta\gamma\delta} + \tau^{\alpha\gamma\delta} L'^{\alpha\gamma\delta}. \end{aligned} \quad (19)$$

For a crystal with one of its facets being a solid-vapor interface, and the others interfaced with the liquid, one can show that

$$V'^\gamma(P^\gamma - P^\alpha) = \frac{2}{3} \left(\sum_{i=1}^{\lambda-2} \sigma_i^{\alpha\gamma} A_i^{\alpha\gamma} + \sigma_{\lambda-1}^{\beta\gamma} A_{\lambda-1}^{\beta\gamma} - \sigma^{\alpha\beta} A_{\lambda-1}^{\beta\gamma} + \sigma_\lambda^{\gamma\delta} A_\lambda^{\gamma\delta} - \sigma^{\alpha\delta} A_\lambda^{\gamma\delta} \right), \quad (20)$$

which makes it possible to represent the reversible work W'_* of formation of a critical crystal by the expression

$$\begin{aligned} W_*^{con} = & \frac{1}{3} \left(\sum_{i=1}^{\lambda-2} \sigma_i^{\alpha\gamma} A_i^{\alpha\gamma} + \sigma_{\lambda-1}^{\beta\gamma} A_{\lambda-1}^{\beta\gamma} - \sigma^{\alpha\beta} A_{\lambda-1}^{\beta\gamma} + \sigma_\lambda^{\gamma\delta} A_\lambda^{\gamma\delta} - \sigma^{\alpha\delta} A_\lambda^{\gamma\delta} \right) + \\ & \tau^{\alpha\beta\gamma} L^{\alpha\beta\gamma} + (\tau^{\beta\gamma\delta} - \tau^{\alpha\beta\delta}) L^{\beta\gamma\delta} + \tau^{\alpha\gamma\delta} L'^{\alpha\gamma\delta}, \end{aligned} \quad (21)$$

or, alternatively, as

$$W_*^{con} = \frac{1}{2} V'_*(P_*^\gamma - P^\alpha) + \tau^{\alpha\beta\gamma} L^{\alpha\beta\gamma} + (\tau^{\beta\gamma\delta} - \tau^{\alpha\beta\delta}) L^{\beta\gamma\delta} + \tau^{\alpha\gamma\delta} L'^{\alpha\gamma\delta}. \quad (22)$$

Equations (21) and (22) are similar to eqs.(12) and (13) which apply to heterogeneous crystal nucleation in the immersion mode. Along with eq.(13), equation (22) will be most useful in later discussions.

The reversible works of heterogeneous formation of crystal nuclei in the immersion and contact modes can now be compared. The difference between the internal pressure of the nucleus and the external pressure does not depend on whether the nucleus forms in the immersed mode (let us denote it by $(P_*^\gamma - P^\alpha)^{imm}$) or in the contact mode (denoted by $(P_*^\gamma - P^\alpha)^{con}$). Indeed, by using equation (9) and the equilibrium condition for the nucleus, namely

$$\mu^\gamma(P^\gamma, T) - \mu^\alpha(P^\alpha, T) = 0, \quad (23)$$

while assuming the crystal to be incompressible, one can show that the difference $P_*^\gamma - P^\alpha$ for the nucleus, in both cases, is determined by the supercooling of the liquid, so that

$$(P_*^\gamma - P^\alpha)^{con} = (P_*^\gamma - P^\alpha)^{imm} = \frac{\Delta h}{v} \ln \Theta, \quad (24)$$

where v is the volume per molecule in the crystal phase. The first equality in eq.(24) is equivalent to

$$\frac{\sigma_{\lambda-1}^{\beta\gamma} - \sigma^{\alpha\beta}}{h'_{\lambda-1}} = \frac{\sigma_{\lambda-1}^{\alpha\gamma}}{h_{\lambda-1}},$$

from which it follows that

$$h'_{\lambda-1} = \frac{\sigma_{\lambda-1}^{\beta\gamma} - \sigma^{\alpha\beta}}{\sigma_{\lambda-1}^{\alpha\gamma}} h_{\lambda-1}. \quad (25)$$

On the other hand, $h_i = h'_i$ for $i = 1, \dots, \lambda - 2, \lambda$, by virtue of eqs.(6), (17), and (24). This means that the Wulff shape of the crystal, in the contact mode, is obtained by simply changing the height of the $\lambda - 1$ -th pyramid of the Wulff crystal in the immersion mode. It is hence clear that if $\sigma_{\lambda-1}^{\beta\gamma} - \sigma^{\alpha\beta} < \sigma_{\lambda-1}^{\alpha\gamma}$, then

$$h'_{\lambda-1} < h_{\lambda-1} \Rightarrow V_*'^\gamma < V_*^\gamma. \quad (26)$$

According to eqs.(13) and (22),

$$W_*^{con} - W_*^{imm} = \frac{1}{2}(V_*'^\gamma - V_*^\gamma)(P_*^\gamma - P^\alpha) + \tau^{\alpha\gamma\delta}(L_\lambda'^{\alpha\gamma\delta} - L_\lambda^{\alpha\gamma\delta}) + (\tau^{\beta\gamma\delta} - \tau^{\alpha\beta\delta})L'^{\beta\gamma\delta} + \tau^{\alpha\beta\gamma}L_{\lambda-1}^{\alpha\gamma\delta}. \quad (27)$$

Because of eqs.(25) and (26), if

$$\sigma_\lambda^{\beta\gamma} - \sigma^{\alpha\beta} < \sigma_\lambda^{\alpha\gamma}, \quad (28)$$

then the first term on the RHS of eq.(27) is negative.

In the case of homogeneous crystal nucleation the line tension contributions to the free energy of crystal nucleus formation are either negligible or non-existent.^{21,22} It allowed one to conclude^{21,22} that if the condition in eq.(28) is fulfilled, it is thermodynamically more favorable for the crystal nucleus to form with its facet λ at the surface rather than within the liquid. Inequality (28) coincides with the condition of partial wettability of the λ -th facet of the crystal by its own liquid phase.²³ This effect has been experimentally observed for water-ice²⁶ at temperatures at or below 0°C. In those experiments,²⁶ when air was added to water vapor the partial

wetting of ice by water transformed into complete wetting, but **only** for some orientations. Besides, the wettability of solids by fluids usually decreases with decreasing temperature.^{34,35} Since the freezing of atmospheric water drops always occurs at temperatures far below 0°C, one can expect the partial wettability of at least some facets of water crystals even in the presence of air. Furthermore, according to Cahn,³⁶ perfect wetting of a solid by a liquid away from the critical point is not generally observed, i.e. the condition in eq.(28) should be fulfilled for most substances. In Cahn’s theory, the general restrictions on the solid phase are that its surface is sharp on an atomic scale and interactions between surface and fluid are sufficiently short-range. Therefore, that theory can be also applied to the case where the temperature is far below the fluid critical point and the solid is of the same chemical nature as the fluid phases. If the temperature approaches the fluid critical temperature, Cahn’s theory becomes inapplicable. However, the temperatures involved in crystallization are usually far below the critical point. All these combined with eq.(28) helps to explain why, in molecular dynamics simulation studies, crystallization begins at or near a surface, and why it is easier, experimentally, to observe the homogeneous crystallization of aerosols than that of the corresponding bulk liquid.

However, the presence of the line tension contribution on the RHS of eq.(27) makes it impossible to draw unambiguous conclusions concerning the difference $W_*^{con} - W_*^{imm}$ for heterogeneous crystal nucleation even when inequality (28) is fulfilled. Although the first term on the RHS of eq.(27) is negative and gives rise to the thermodynamic propensity of the crystal nucleus to form with the facet $\lambda - 1$ at the droplet surface, the line tension contributions can be both negative and positive because any of the line tensions involved can be either negative or positive.^{31–33} Moreover, the sign of the line tension may change depending on the temperature at which the crystallization occurs.

3 Numerical evaluations and discussions

To illustrate the above theory by numerical evaluations, consider first the homogeneous freezing of water droplets (surrounded by water vapor in air) at around $T_{hm} = 233$ K (i.e., about -40°C). The estimates for homogeneous crystal nucleation will serve as a reference point to obtain some estimates of the relative importance of the line tension contributions on the RHS of eq.(27) for $W_*^{con} - W_*^{imm}$.

As reported by Defay *et al.*²³, the rate of homogeneous crystal nucleation in bulk supercooled water at this temperature is $7 \times 10^{12} \text{cm}^{-3} \text{s}^{-1}$, with the nucleation barrier height $W_* = 45 kT_{hm}$, the average (over all crystal facets) surface tension of liquid-solid (water-ice) interface $\sigma^{\alpha\gamma}$ being about 20 dyn/cm (Table 18.1 in ref.23). The surface tensions of liquid-vapor and solid-vapor (ice-water vapor) interfaces at $T_{hm} = 233$ K will be taken to be $\sigma^{\alpha\beta} = 88$ dyn/cm and $\sigma^{\beta\gamma} = 103$ dyn/cm, respectively. All these values of $\sigma^{\alpha\gamma}$, $\sigma^{\alpha\beta}$, and $\sigma^{\beta\gamma}$ are consistent with the data provided in ref.2.

Let us assume that only the basal facets of the hexagonal ice crystal is partially wettable by water at $T_{hm} = 233$ K. The height of the basal pyramid of the crystal cluster will be denoted by \tilde{h}_b when the basal facet is at the droplet surface (hereafter a tilde will mark quantities for this case) and by h_b when the entire crystal is immersed in the droplet. The corresponding works of homogeneous formation of crystal nuclei will be denoted as \widetilde{W}_* and W_* . According to eqs.(31) and (32) of ref.21 and eqs.(15) and (16) of ref.22, one can obtain for crystal nuclei: $h_* \equiv 2h_b \simeq 21 \times 10^{-8}$ cm, $\tilde{h}_* \equiv \tilde{h}_b + h_b \simeq 18 \times 10^{-8}$ cm, $\widetilde{W}_* \simeq 39.3 kT_{hm}$, $\Delta W_* \equiv \widetilde{W}_* - W_* \approx -5.7 kT_{hm}$

These evaluations are for homogeneous crystal nucleation in the volume-based vs surface-stimulated modes^{21,22} which are equivalent to the immersion and contact modes, respectively, of the heterogeneous crystal nucleation. At any particular temperature, the critical crystal of heterogeneous nucleation is much smaller than for homogeneous nucleation. On the other hand,

the size of the nucleus increases with increasing temperature (i.e., decreasing supercooling). Thus, one can expect that for any foreign particle there exists a temperature $233 \text{ K} < T_{ht} < 273 \text{ K}$ such that the linear size of the crystal nucleus (hence the number of molecules therein, ν_c) for heterogeneous nucleation is comparable to that estimated above for homogeneous nucleation at $T_{hm} = 233 \text{ K}$. The energy unit $k_B T$ (k_B is the Boltzmann constant) varies from $3.2 \times 10^{-14} \text{ erg}$ to $3.8 \times 10^{-14} \text{ erg}$, i.e, by about 10 %.

Let us assume, that for a selected foreign particle the temperature $T_{ht} \simeq 253 \text{ K}$ with the thermal energy unit $k_B T_{ht} \simeq 3.5 \times 10^{-14} \text{ erg}$. At this temperature, the first term on the RHS of eq.(27) (hereafter referred to as the “surface-stimulation term”) can be roughly assumed to be equal to ΔW_* because both quantities represent the surface contribution to the difference between the free energy of nucleus formation in the surface-stimulated and volume-based modes (for heterogeneous and homogeneous nucleation, respectively). Thus, according to the above estimates,

$$\frac{\frac{1}{2}(V_*'^\gamma - V_*^\gamma)(P_*^\gamma - P^\alpha)}{k_B T_{ht}} \approx \frac{\Delta W_*}{k_B T_{ht}} \approx -5.7 \frac{T_{hm}}{T_{ht}} \approx -5.3. \quad (29)$$

As mentioned above, this contribution is negative if facet $\lambda - 1$ (formed at the liquid-vapor interface) is only partially wettable by its melt (i.e., water), which is the case with the basal facet of the crystals of hexagonal ice. Consequently, the droplet surface always makes the contact mode of heterogeneous crystal nucleation in water droplets thermodynamically more favorable than the immersion mode, regardless of the nature of the foreign particle.

It is virtually impossible to provide general unambiguous estimates for the line tension contributions to $W_*^{con} - W_*^{imm}$ in eq.(27). Indeed, the line tension is notorious not only for the lack of reliable experimental data but (mostly) for its ability of being both negative and positive and take values in the range from 10^{-1} to 10^{-5} erg (see, e.g., refs.31-33). Nevertheless, some estimates can provide useful insight into the problem of “contact mode vs immersion mode” of

heterogeneous crystal nucleation.

In the second term on the RHS of eq.(27), the difference $L'^{\alpha\gamma\delta} - L^{\alpha\gamma\delta}$ represents the difference between the lengths of the “liquid-crystal-foreign particle” contact line in the contact and immersion modes. Clearly, this difference is negative. Considering, as above, that it is the basal facet of the hexagonal ice crystal which forms at the liquid-vapor interface (with one of the six prismatic facets formed on the foreign particle), one can conclude that $L'^{\alpha\gamma\delta} - L^{\alpha\gamma\delta} \approx -a = -8.65 \times 10^{-8}$ cm for $q = 2$ and $L'^{\alpha\gamma\delta} - L^{\alpha\gamma\delta} \approx -a = -13.8 \times 10^{-8}$ cm for $q = 0.5$. As for the line tension $\tau^{\alpha\gamma\delta}$, its sign can be expected to be positive,^{31–33} but we are not aware of any experimental or theoretical data reported for “foreign particle-crystal-vapor” three-phase contact regions. Assuming that $\tau^{\alpha\gamma\delta}$ can be anywhere in the range from 10^{-1} erg to 10^{-5} erg, it is still most likely to be closer to 10^{-5} than to 10^{-1} erg because two out of three phases in contact are solid phases involving little inhomogeneities of density profiles in the contact region. Thus, one can cautiously suggest that: a) this three-phase contact line impedes the heterogeneous crystal nucleation in the immersion mode vs contact mode; b) possible values of the term $\tau^{\alpha\gamma\delta}(L'^{\alpha\gamma\delta} - L^{\alpha\gamma\delta})/k_B T$ may be somewhere in the range from -100 to -10 .

The third term on the RHS of eq.(27) is due to the three-phase contact line “liquid-vapor-foreign particle”. The length of this line, $L^{\beta\gamma\delta}$, is equal to $-(L'^{\alpha\gamma\delta} - L^{\alpha\gamma\delta})$, evaluated in the above paragraph, i.e., $L^{\beta\gamma\delta} \approx 8.65 \times 10^{-8}$ cm for $q = 2$ and 13.8×10^{-8} cm for $q = 0.5$. Further, the density inhomogeneities in the “foreign particle-crystal-vapor” contact region can be expected to be negligible compared to those in the “foreign particle-crystal-liquid”, “liquid-vapor-foreign particle”, or “liquid-vapor-liquid”. Therefore, one can consider that the line tension $\tau^{\beta\gamma\delta}$ is negligible when compared to $\tau^{\alpha\beta\delta}$, so that the third term becomes $(\tau^{\beta\gamma\delta} - \tau^{\alpha\beta\delta})L^{\beta\gamma\delta} \simeq -\tau^{\alpha\beta\delta}L^{\beta\gamma\delta}$. Depending on the wettability of the foreign particle by liquid water in the water vapor, $\tau^{\alpha\beta\delta}$ can be positive as well as negative. It was noted, however, that for the

same foreign particle to be able to serve as an equilibrium nucleating center in both immersion and contact modes it has to be completely wettable by water. Thus, one can suggest^{27–29} that the line tension $\tau^{\alpha\beta\delta} < 0$ with its absolute value closer to 10^{-5} than 10^{-1} . Besides, the third term on the RHS of eq.(27) can be expected to provide a contribution to $W_*^{con} - W_*^{imm}$ which is close to the contribution from the second term in absolute value and has an opposite sign. The approximate compensation of the second and third terms can thus be expected.

The last term on the RHS of eq.(27) is due to the three-phase contact line “liquid-vapor-crystal”. Considering again the basal facet of the hexagonal ice crystal forms at the liquid-vapor interface (with one of the six prismatic facets on the foreign particle), the length of this contact line is approximately $L^{\alpha\beta\gamma} \approx 5a$, that is, $L^{\alpha\beta\gamma} \approx 40.2 \times 10^{-8}$ cm for $q = 2$ and $L^{\alpha\beta\gamma} \approx 69.0 \times 10^{-8}$ cm for $q = 0.5$. As the basal facet of an Ih crystal is partially wettable by liquid water with the contact angle (measured inside the liquid phase) less than $\pi/2$, one can consider $\tau^{\alpha\beta\gamma}$ to be negative.^{31,32} Even assuming for the value of $\tau^{\alpha\beta\gamma}$ the smallest experimentally reported order of magnitude, 10^{-5} erg, one can conclude that: a) this contact line significantly enhances the contact mode of heterogeneous crystal nucleation compared to the immersion mode; b) the absolute value of the line tension contribution to $W_*^{con} - W_*^{imm}$ from the “vapor-liquid-ice” contact line is *at least* by one order of magnitude greater than that of the surface-stimulation term (first term on the RHS of eq.(27)). Thus, this line tension contribution to $W_*^{con} - W_*^{imm}$ can dominate the surface-stimulation term.

Evaluations for the case where the nucleus of an Ih crystal is formed a) in the immersion mode with the basal facet on the foreign particle and b) in the contact mode with the basal facet on the particle and one of its prismatic facets at the droplet-vapor interface can be carried out in a similar fashion. Besides one can consider the case where in the contact mode one prismatic facet forms on the foreign particle and another at the droplet surface. Curiously, in

this situation the foreign particle does not even have to be in contact with the droplet surface. Moreover, the crystal nucleus may form with one of its basal facets on the foreign particle and the other at the droplet surface, and in this case, the foreign particle cannot be in contact with the droplet surface at all (unless it has a very irregular, non-compact shape). In the latter case, the term “contact mode” is not even appropriate. Two common features of all these “contact mode” situations are that: a) one of the crystal facets always forms at the droplet surface; b) there always exists a contact “vapor-liquid-crystal” of three water phases. Both of these factors (the latter even significantly stronger than the former) thermodynamically favor the formation of a crystal nucleus in the compact mode compared to the immersion one. The correctness of the term “contact mode” becomes, however, questionable, at least from a thermodynamic standpoint. One trivial exception from the above consideration is the case where the surface of the foreign particle touches the liquid-vapor interface from outside in parallel orientation (see Fig.1, case 4). In this situation the same facet of the crystal nucleus forms at the droplet surface and on the foreign particle, and there is no thermodynamic advantage for this mode compared to the immersion mode (when the crystal nucleus forms with the same facet on the same surface of the foreign particle).

It is worth emphasizing that for accurate calculations of W_*^{imm} and W_*^{con} it is necessary to know not only the physico-chemical characteristics of the forming crystals (such as Δh , σ 's and τ 's, etc...) but also the shape and size of the crystal nuclei. The latter, however, can be accurately determined analytically if the former are known.

Indeed, the shape of the crystal nucleus is determined by Wulff's relations (5) and (16). For example, since the shape of an ice crystal cluster is known (assumed to be a hexagonal prism), its state is completely determined by two geometric variables (provided that its density and temperature are given), e.g., the height of the prism and the length of a side of a (regular)

hexagon (the base of the prism). However, owing to Wulff's relations, eqs.(5) and (16), only one of these two variables is independent. Therefore, both works W^{imm} and W^{con} are functions of only one independent variable, say, variable a , the length of a side of the hexagon. The concrete form of the functions $W^{imm} = W^{imm}(a)$ and $W^{con} = W^{con}(a)$ depends on the mutual orientation and location of the crystal cluster and foreign particle (and droplet surface in case of W^{con}).

For instance, consider a crystal cluster formed with one of its basal facets on a foreign particle in the immersion mode. For the contact mode, let us consider the same basal facet on the foreign particle and a prismatic facet (assumed to be only partially wettable by water) at the droplet surface. Mark the basal facets with subscripts 1 and 8 and the prismatic facets with subscripts 2, ..., 7 (Figure 5).

As agreed upon above, facet 8 forms on the foreign particle. Clearly, in the immersion mode $\sigma_p^{\alpha\gamma} \equiv \sigma_2^{\alpha\gamma} = \dots = \sigma_7^{\alpha\gamma}$, $A_p^{\alpha\gamma} \equiv A_2^{\alpha\gamma} = \dots = A_7^{\alpha\gamma}$, $A_b^{\alpha\gamma} \equiv A_1^{\alpha\gamma} = A_8^{\alpha\gamma}$. In the contact mode the prismatic facet 7 (assumed to be only partially wettable by liquid water) represents the crystal-vapor interface, hence $\sigma_p^{\alpha\gamma} \equiv \sigma_2^{\alpha\gamma} = \dots = \sigma_6^{\alpha\gamma}$, $\sigma_p^{\beta\gamma} = \sigma_7^{\beta\gamma}$. Unlike the crystal cluster in the immersion mode, the basal facet in the contact mode is not a regular hexagon, $A_b'^{\alpha\gamma} \equiv A_1'^{\alpha\gamma} = A_8'^{\alpha\gamma}$ and $A_b'^{\alpha\gamma} < A_b^{\alpha\gamma}$, i.e., the surface areas of the basal facets in the contact mode is smaller than that in immersion mode, according to eq.(25). Let us mark two prismatic facets adjacent to facet 7 by subscripts 2 and 6. Clearly, $A_p^{\alpha\gamma} = A_3^{\alpha\gamma} = A_4^{\alpha\gamma} = A_5^{\alpha\gamma}$, $A_p'^{\alpha\gamma} \equiv A_2^{\alpha\gamma} = A_6^{\alpha\gamma} < A_p^{\alpha\gamma}$, $A_p^{\beta\gamma} \equiv A_7^{\beta\gamma} > A_7'^{\beta\gamma}$ (both inequalities are again due to eq.(25)).

Let us use a_i and a_i' ($i = 2, \dots, 7$) to denote the length of the edge formed by the basal facet with prismatic facet i in the immersion and contact modes, respectively. In the immersion mode the base is a regular hexagon, i.e., $a \equiv a_2 = \dots = a_7$. As clear from eq.(25), in the contact mode $a_2' = a_6' < a$, $a_7' > a$, whereas $a_3' = a_4' = a_5' = a$.

In the first term on the RHS's of eqs.(10) and (19) the number of molecules in the crystal cluster can be represented as $\nu = \rho^\gamma V^\gamma$ or $\nu = \rho^\gamma V'^\gamma$, respectively, where ρ^γ is the number density of molecules in phase γ (ice). The volume of an Ih crystal (shaped as a hexagonal prism) is equal to the product “height of the prism” \times “surface area of the base”. In both the immersion and contact modes the surface area of the base (regular hexagon in the former and irregular in the latter) is proportional to a^2 , although coefficients of proportionality are different. In both cases, the height of the prism, h , is linearly related to a according to Wulff's relations (5) and (16), respectively. Thus, in both eqs.(10) and (19) $\nu \propto \rho^\gamma a^3$. Likewise, one can show that all the surface tension and line tension terms on the RHS's of eqs.(10) and (19) are proportional to a^2 and a , respectively. Therefore, the reversible works of formation of a crystal cluster in these modes can be written (tedious but simple algebra is omitted) as

$$W^{imm}(a) = -I_3 a^3 + I_2 a^2 + I_1 a, \quad W^{con}(a) = -C_3 a^3 + C_2 a^2 + C_1 a, \quad (30)$$

where I_3 , I_2 , I_1 and C_3 , C_2 , C_1 are positive coefficients,

$$I_3 = \frac{9}{4} \rho^\gamma \Delta h \ln(\Theta) (\sigma_b^{\alpha\gamma} + \sigma_b^{\gamma\delta} - \sigma^{\alpha\delta}) / \sigma_p^{\alpha\gamma}, \quad I_2 = \frac{3\sqrt{3}}{2} [2\sigma_b^{\alpha\gamma} + 3(\sigma_b^{\gamma\delta} - \sigma^{\alpha\delta})], \quad I_1 = 6\tau^{\alpha\gamma\delta},$$

and

$$\begin{aligned} C_3 &= \rho^\gamma \Delta h \ln(\Theta) \left(\frac{3\sqrt{3}}{2} - C_h + \frac{C_h^2}{\sqrt{3}} \right) \frac{\sqrt{3}}{2} (\sigma_b^{\alpha\gamma} + \sigma_b^{\gamma\delta} - \sigma^{\alpha\delta}) / \sigma_p^{\alpha\gamma}, \\ C_2 &= (\sigma_b^{\alpha\gamma} + \sigma_b^{\gamma\delta} - \sigma^{\alpha\delta}) \left(\frac{3\sqrt{3}}{2} - C_h + \frac{C_h^2}{\sqrt{3}} \right) + \\ &\quad \left[(5 - 2(1 - (\sigma_p^{\beta\gamma} - \sigma^{\alpha\beta}) / \sigma_p^{\alpha\gamma})) \sigma_p^{\alpha\gamma} + (\sigma_p^{\beta\gamma} - \sigma^{\alpha\beta}) (2 - (\sigma_p^{\beta\gamma} - \sigma^{\alpha\beta}) / \sigma_p^{\alpha\gamma}) \right] \frac{\sqrt{3}}{2} (\sigma_b^{\alpha\gamma} + \sigma_b^{\gamma\delta} - \sigma^{\alpha\delta}) / \sigma_p^{\alpha\gamma}, \\ C_1 &= (\tau^{\beta\gamma\delta} - \tau^{\alpha\beta\delta}) (2 - (\sigma_p^{\beta\gamma} - \sigma^{\alpha\beta}) / \sigma_p^{\alpha\gamma}) + \tau^{\alpha\gamma\delta} (5 - 2(1 - (\sigma_p^{\beta\gamma} - \sigma^{\alpha\beta}) / \sigma_p^{\alpha\gamma})) + \\ &\quad \tau^{\alpha\beta\delta} (2C_h + (2 - (\sigma_p^{\beta\gamma} - \sigma^{\alpha\beta}) / \sigma_p^{\alpha\gamma})), \end{aligned}$$

with

$$C_h = \frac{\sqrt{3}}{2} \left(1 - \frac{\sigma_p^{\beta\gamma} - \sigma^{\alpha\beta}}{\sigma_p^{\alpha\gamma}} \right)$$

and ρ^γ is the number density of molecules in the crystal phase.

Using eq.(30), one can find the length a_* of a side of the hexagonal base of the crystal nucleus as the positive solution of the equation $dW^{imm}(a)/da|_{a_*} = -3I_3a_*^2 + 2I_2a_* + I_1 = 0$, or alternatively, $dW^{con}(a)/da|_{a_*} = -3I_3a_*^2 + 2I_2a_* + I_1 = 0$. which lead to $a_* = (2I_2 + \sqrt{4I_2^2 + 12I_1I_3})/6I_3$ or $a_* = (2C_2 + \sqrt{4C_2^2 + 12C_1C_3})/6C_3$ (see two paragraphs above eq.(30)). The height of the crystal nucleus (shaped as a hexagonal prism) is the same in both immersion and contact modes, $h_* = a_* \frac{\sqrt{3}}{2} (\sigma_b^{\alpha\gamma} + \sigma_b^{\gamma\delta} - \sigma^{\alpha\delta}) / \sigma_p^{\alpha\gamma}$.

To numerically evaluate a_* and h_* , information on $\rho, \Delta h, \sigma^{\alpha\beta}, \sigma^{\alpha\delta}, \sigma_b^{\alpha\gamma}, \sigma_p^{\alpha\gamma}, \sigma_b^{\gamma\delta}, \sigma^{\beta\gamma})_p, \tau^{\alpha\beta\gamma}, \tau^{\alpha\beta\delta}, \tau^{\alpha\gamma\delta}$, and $\tau^{\beta\gamma\delta}$ is needed. Experimental data on $\rho^\gamma, \Delta h$, and $\sigma^{\alpha\beta}$ are readily available (even as functions of temperature). For our evaluations they were taken to be $\rho^\gamma = 0.92N_A/18 \text{ cm}^{-3}$, $\Delta h \simeq 333.55 \times 10^7 N_A/18 \text{ erg}$ (where N_A is the Avogadro constant), and $\sigma^{\alpha\beta} = 83 \text{ dyn/cm}$. Some data on $\sigma_b^{\alpha\gamma}$ and $\sigma_p^{\alpha\gamma}$ as well as on the mean value of the crystal-vapor surface tension have been also reported (see ref.2 for a short review). However, virtually no reliable data are currently available for any solid-ice interfacial tensions and line tensions in “solid substrate-ice-liquid water-water vapor” systems. These were hence chosen somewhat arbitrarily, the main criterion being a reasonable agreement of the estimates extracted from the above equations with those obtained from the experimental data on homogeneous ice nucleation. Considering nucleation of ice crystals on a foreign particle such that at a given temperature $\sigma^{\alpha\delta} = 40 \text{ dyn/cm}$, $\sigma_b^{\alpha\gamma} = 23 \text{ dyn/cm}$, $\sigma_p^{\alpha\gamma} = 24 \text{ dyn/cm}$, $\sigma_b^{\gamma\delta} = 50 \text{ dyn/cm}$, $\sigma^{\beta\gamma})_p = 102 \text{ dyn/cm}$, $\tau^{\alpha\beta\gamma} = -10^{-4} \text{ dyn}$, $\tau^{\alpha\beta\delta} = 7 \times 10^{-5} \text{ dyn}$, $\tau^{\alpha\gamma\delta} = 10^{-5} \text{ dyn}$, and $\tau^{\beta\gamma\delta} = 5 \times 10^{-6} \text{ dyn}$ (reasonable choice according to scarce data available in literature), equations for a_* and h_* would provide $a_* \simeq 29 \times 10^{-8} \text{ cm}$, $h_* \simeq 35 \times 10^{-8} \text{ cm}$, and $W_*^{con} - W_*^{imm} \simeq -12k_B T_{ht}$. As intended, these values are consistent with the estimates obtained above from the experimental data on the homogeneous nucleation rate.

4 Concluding Remarks

Previously, in the framework of CNT a criterion was found for when the surface of a droplet can stimulate crystal nucleation therein so that the formation of a crystal nucleus with one of its facets at the droplet surface is thermodynamically favored (i.e., occurs in a surface stimulated mode) over its formation with all the facets *within* the liquid phase (i.e., in a volume-based mode). For both unary²¹ and multicomponent²² droplets, this criterion coincides with the condition of partial wettability of at least one of the crystal facets by the melt (the contact angle, measured inside the liquid phase, must be greater than zero).

However complex a theory of homogeneous crystal nucleation in droplets may be, the presence of foreign particles, serving as nucleating centers, makes the crystal nucleation phenomenon (and hence its theory) even more involved. Numerous aspects of heterogeneous crystal nucleation still remain obscure. One of most intriguing problems in this field remains the strong enhancement of heterogeneous crystallization in the contact mode compared to the immersion one. It has been observed that the same nucleating center initiates the crystallization of a supercooled droplet at a higher temperature in the contact mode (with the foreign particle just *in contact* with the droplet surface) compared to the immersion mode (particle *immersed* in the droplet).² Many heterogeneous centers have different nucleation thresholds when they act in contact or immersion modes, indicating that the mechanisms may be actually different for the different modes. Underlying physical reasons for this enhancement have remained largely unclear, but the phenomenon of surface-stimulated (homogeneous) crystal nucleation had strongly suggested that the droplet surface could enhance heterogeneous nucleation in a way similar to the enhancement of the homogeneous process.

In this paper we have extended the approach, previously developed in refs.21,22, to heterogeneous crystal nucleation on a solid particle (in both immersion and contact modes) and have

presented a thermodynamic model shedding some light on the mechanism of the enhancement of this process in the contact mode. Our thermodynamic analysis suggests that the droplet surface can indeed thermodynamically enhance crystal nucleation in the contact mode compared to the immersion mode. Whether this occurs or not for a particular foreign particle is determined, however, by the interplay between various surface tensions and four line tensions involved in this process. As clear from our model, the droplet surface may stimulate the heterogeneous crystal nucleation even in the case where the foreign particle is actually completely immersed therein, but is situated closely enough to the surface. This suggests that the term “contact mode enhancement” is probably not very appropriate for this phenomenon.

As a numerical illustration of the proposed model, we have considered heterogeneous nucleation of Ih crystals on generic macroscopic foreign particles in water droplets at $T = 253$ K. Our results suggest that while the droplet surface always stimulates crystal nucleation on foreign particles in the “contact mode”, the line tension contribution to this phenomenon (due to the contact of three water phases, “vapor-liquid-crystal”) may be as important as the surface tension contribution.

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Captions

to Figures 1 to 5 of the manuscript

“THERMODYNAMICS OF HETEROGENEOUS CRYSTAL NUCLEATION IN CONTACT AND IMMERSION MODES” by **Y. S. Djikaev and E. Ruckenstein**

Figure 1. Heterogeneous crystal nucleation in a liquid droplet surrounded by vapor. “Immersion” mode: the crystal cluster forms with one of its facets on a foreign particle, completely immersed in a liquid droplet; all other crystal facets interface the liquid. “Contact” mode: the foreign particle is in contact with the droplet surface; the cluster forms with one of the crystal facets on the particle, another facet at the liquid-vapor interface, and all other facets making the “crystal-liquid” interface. Cases 1 through 4 represent a few of possible variations of the “foreign particle–droplet surface” contact.

Figure 2. Illustration to Wulff’s relations. The surface area and surface tension of facet i are denoted by A_i and σ_i , respectively; h_i is the distance from facet i to reference point O .

Figure 3. Heterogeneous formation of a crystal nucleus on a foreign particle completely immersed in the liquid.

Figure 4. Heterogeneous formation of a crystal nucleus on a foreign particle in contact with the liquid-vapor interface.

Figure 5. Heterogeneous formation of an Ih cluster on a foreign particle in the immersion and contact modes. contact with the liquid-vapor interface. The crystal cluster has a shape of a hexagonal prism. One of the basal facets (facet 8) is formed on the foreign particle, the other (facet 1) interfaces the liquid. Two of the prismatic facets (with numbers 4 and 7) lie in the plane perpendicular to the Figure. Prismatic facets 5 and 6 cannot be seen by the reader, so they are shown in the parentheses.

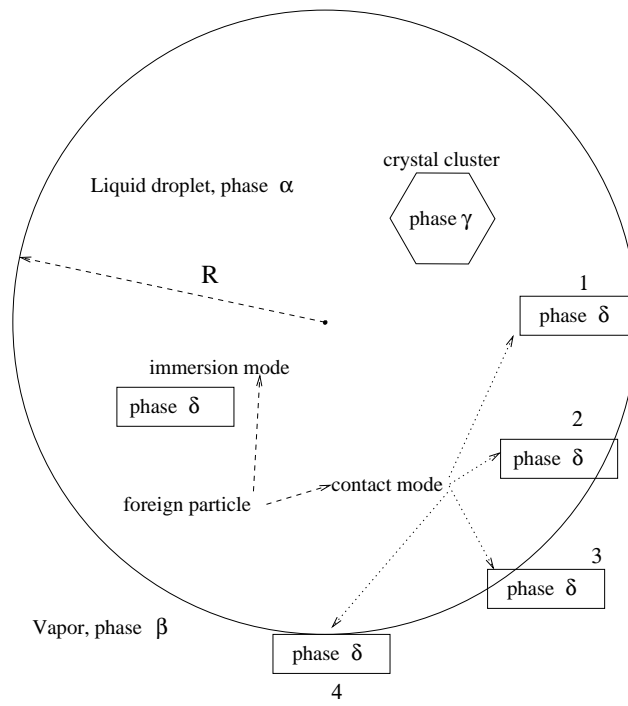


Figure 1:

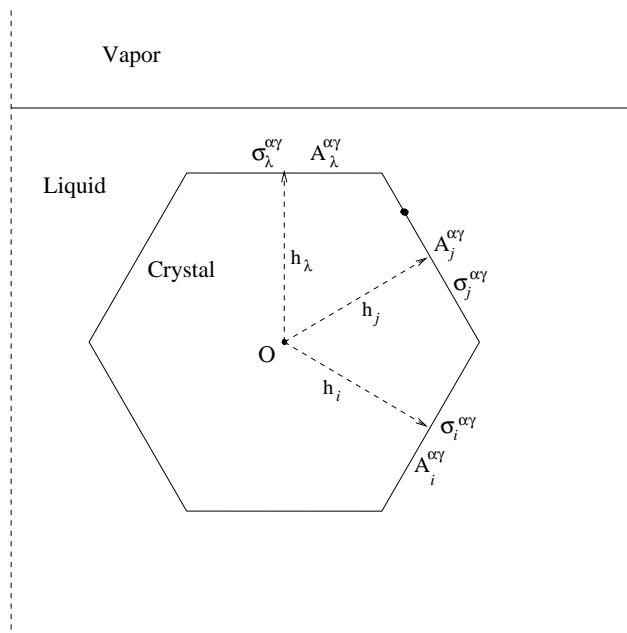


Figure 2:

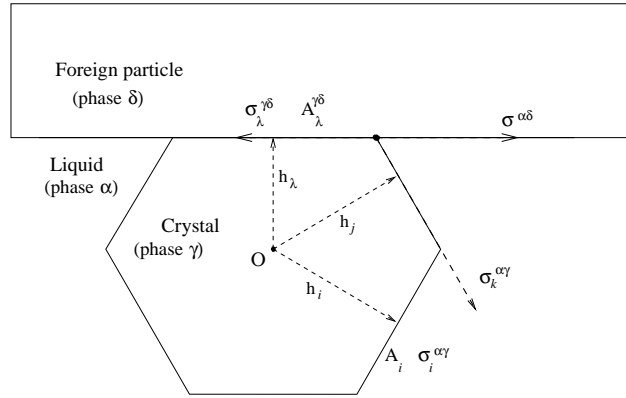


Figure 3:

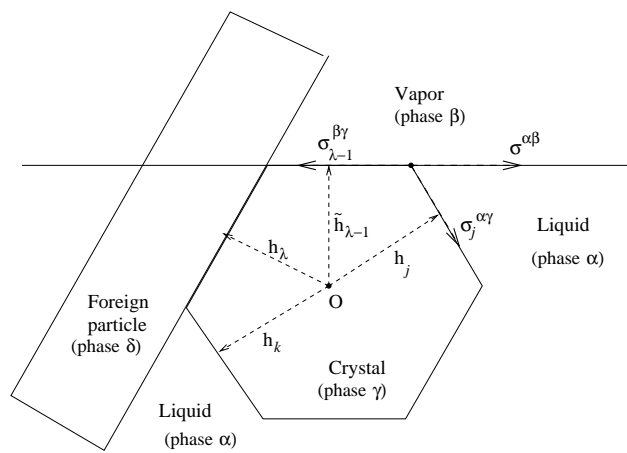


Figure 4:

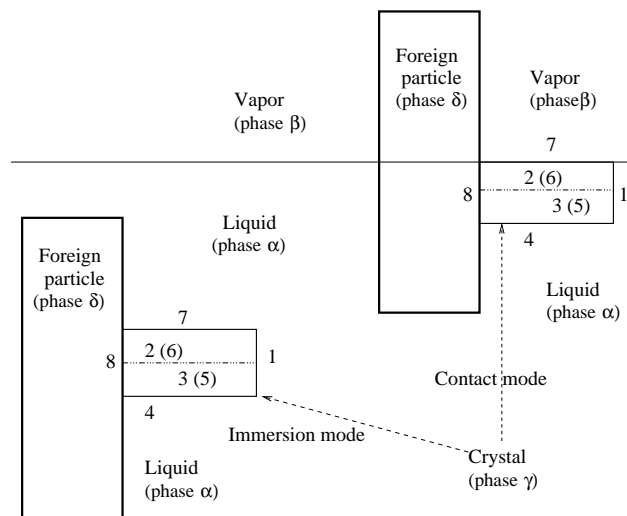


Figure 5: